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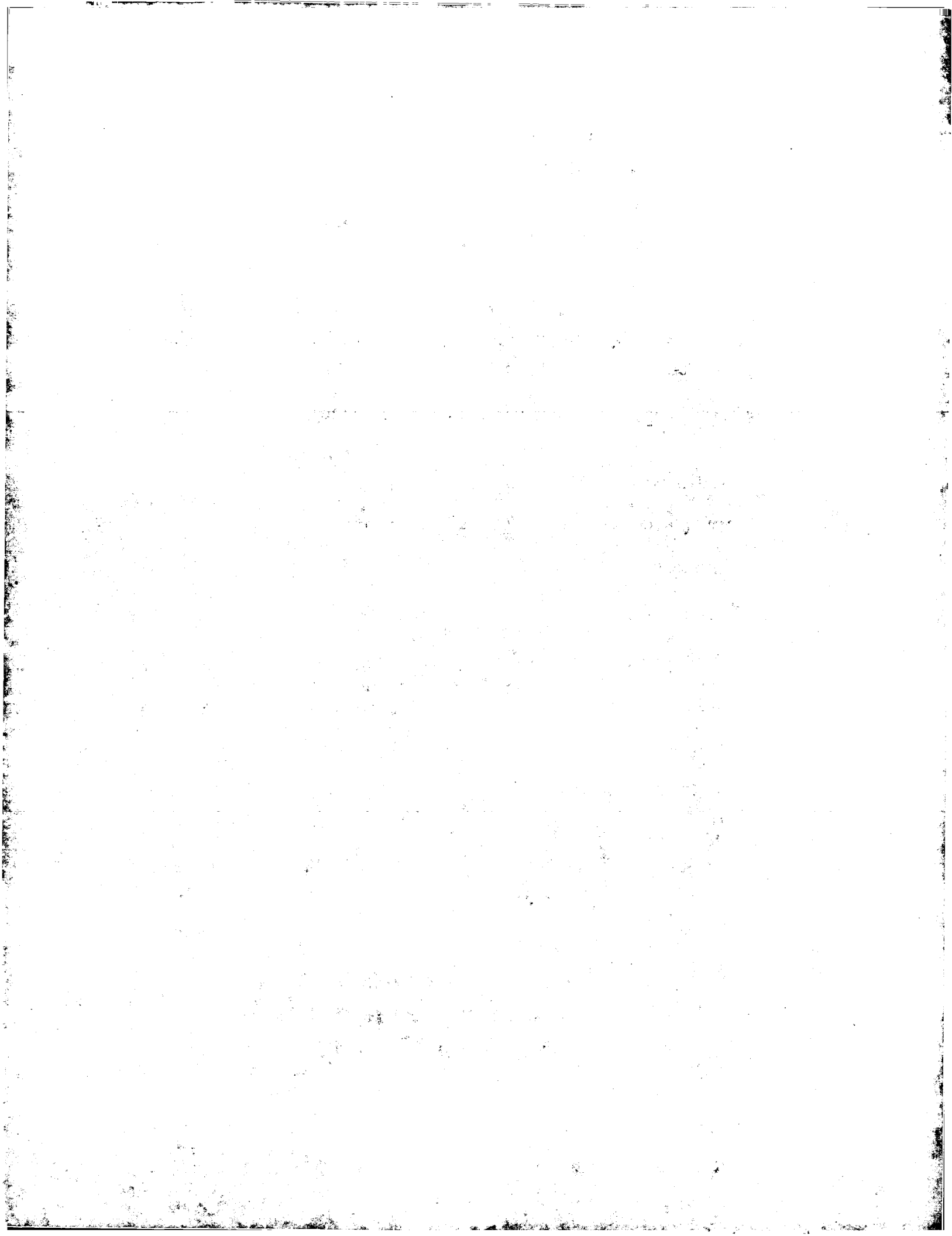
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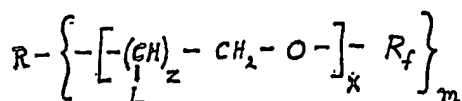
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## (54) FLUOROCARBON SURFACTANTS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

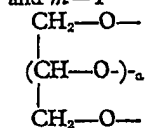
This invention relates to novel compounds containing fluoroalkyl groups. According to the present invention we provide novel compounds having the general formula



wherein  $R_f$  is either  $-\text{CF}=\text{CF}-(\text{CF}_2)_n\text{F}$  or  $-\text{CF}_2-\text{CFH}-(\text{CF}_2)_n\text{F}$  in which  $n=0$  to 10  
 $\text{L}$  is H or  $\text{CH}_3$   
 $x$  is 2 to 40  
 $z$  is 0, 1 or 2

and  $R$  and  $m$  are selected from

$R_f\text{O}-$  (wherein  $R_f$  is as hereinbefore defined)  
 and  $m=1$



and  $m=a+2$

where  $a$  is zero or an integer from one to four.

$-\text{O}-$  and  $m=2$   
 $R'-\text{O}-$  and  $m=1$   
 $R'-\text{CO}-\text{O}-$  and  $m=1$   
 $R'-\text{N}<$  and  $m=2$   
 and  
 $R'-\text{S}-$  and  $m=1$

wherein  $R'$  is an allyl, alkyl, alkyl phenyl or alkyl naphthyl group, the alkyl group in each containing zero, 1 or 2 carbon atoms. When any substituent represented by a given symbol occurs more than once in any compound thus

specified, the said substituents may be the same or different.

The group  $R_f$ , being a highly fluorinated group and therefore a group having oleophobic and hydrophobic properties, confers on the compounds the ability to modify the surface properties of materials. The materials to which the novel compounds are applied may be liquid or solid and the novel compounds may be either applied to the surface or mixed into the bulk from which they tend to migrate to the surface. The presence of these novel compounds at a surface lowers the surface-free energy and thus they are useful in many applications where surface-active properties are desirable, for example wetting, emulsification, anti-friction, anti-static, anti-adhesion and oil-repellent properties.

The compounds of the present invention are preferably applied to a surface from a solution, suspension or other mixture with a diluent which facilitates the said application of the compound to the surface.

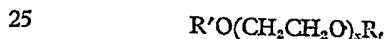
The compounds of this invention are especially useful as mould-release agents, for example in thermoplastic polymer mouldings, especially hydrocarbon polymers, e.g. polyethylenes and polypropylenes. Accordingly the invention also provides a composition for the release of thermoplastic mouldings comprising a compound as provided in the present invention and a propellant suitable for the discharge of the composition from an aerosol container.

The group  $R_f$  is preferably a short group in which  $n$  is less than five and the compounds wherein  $n$  is 0 or 1 are especially preferred on account of their relative cheapness and ease of preparation. When  $n=0$  the fluoroalkyl group  $R_f$  may be derived from tetrafluoroethylene and the compound is observed to contain almost exclusively the group  $-\text{CF}_2\text{CH}_2\text{H}$ .

The oxyalkylene group confers on the compounds the ability to wet and conform to surfaces, especially hydrophilic surfaces. The oxyalkylene groups preferred are those where-

in the integer  $z$  is unity and the polyoxyalkylene group is then a single unbranched chain of ethylene oxide or propylene oxide units,  $L$  being hydrogen and/or methyl respectively. The length of the oxyalkylene chain is not critical to the utility of the compounds and may be chosen to constitute a convenient balance between the hydrophilic properties of such a chain and the hydrophobic properties of the fluoroalkyl group. The number of oxyalkylene units in the chain denoted by  $x$  may be an average number and  $x$  need not be an integral value. The preferred values of  $x$  are generally from 4 to 30 and, when the fluoroalkyl groups are short, values of  $x$  from 4 to 15 are especially preferred.

From the standpoint of ease and cost of manufacture of the compounds the group  $R$  is preferably a fluorinated group  $R_f-O-$  as described above or a group  $R'-O-$  wherein  $R'$  is an allyl, alkyl, alkyl phenyl or alkyl naphthyl group wherein the alkyl group in each contains zero, 1 or 2 carbon atoms. Especially preferred is a compound of formula



wherein  $R'$  is a methyl group and  $R_f$  and  $x$  are as hereinbefore defined.

For some applications, e.g. emulsification, it may be desirable to incorporate two polyoxyalkylene chains and when such compounds are required the above groups  $R'-N<$  or  $R'CO-N<$  are the preferred groups.

One preferred method for the preparation of the novel compounds of the present invention is by means of a reaction between a straight-chain terminally-unsaturated perfluoroolefine ( $C_nF_{2n+4}$  where  $n$  is 0 to 10 and preferably 0 or 1 as previously defined) and a compound containing a chain of repeating oxyalkylene groups, the chain terminating in at least one hydroxyl group. Oxyalkylene compounds of the above type are readily available, for example from the reaction between a polyglycol or a condensation product of ethylene oxide, propylene oxide, or formaldehyde and an appropriate compound containing active hydrogen, e.g. an alcohol, phenol, wherein one end of the product terminates in an alkoxyl phenoxyl, alkyl phenoxyl or alkenoxyl group.

Reaction between the perfluoroolefine and the hydroxyl end of the oxyalkylene compound is effected by the presence of a basic compound, preferably an inorganic basic compound for example sodium and potassium salts of weaker inorganic acids, especially carbonic, silicic and phosphoric acids.

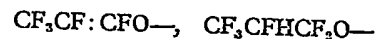
Alternatively the perfluoroolefine may be reacted with an alkali-metal derivative of the oxyalkylene compound, preferably a sodium or potassium derivative which may be prepared for example by the action of sodium or potassium hydride on the oxyalkylene compound. The oxyalkylene compound may term-

inate in one hydroxy and one hydrocarbon group or in two hydroxy groups. The hydroxy groups only are reactive to the perfluoroolefine and therefore either one or two fluorocarbon groups may be present in the product depending on the structure of the starting material.

The invention is illustrated by the following Examples:

#### Example 1.

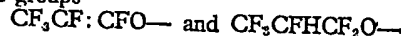
An autoclave charged with potassium carbonate (14g), methyl ethyl ketone (100 ml) and polyethylene glycol-1000 (50g) was purged with nitrogen. The mixture was stirred and hexafluoropropene was injected. An exothermic reaction occurred and the pressure fell. Hexafluoropropene was injected successively until a total pressure drop of 1200 psig was recorded. The reaction product was filtered and two layers formed, the lower of which was separated and identified as a mixture of oligomers of hexafluoropropene (43g). The solvent was pumped from the upper layer using a rotary evaporator and there was obtained a viscous yellow brown oil which solidified on cooling (60.5g). Infra-red spectroscopy showed the absence of  $-OH$  groups and the presence of  $C-F$  bonds and the oxyethylene chain in this material. Nuclear magnetic resonance showed the presence of the groups



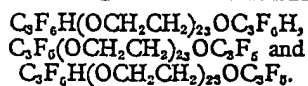
in the ratio 2:9 respectively and elemental fluorine analysis indicated that the product contained a fluoroalkyl group on each end of the polyethylene glycol chain. A small proportion of  $C_6F_{11}$  fluoroalkenyl groups were also detected in the product.

#### Example 2.

An autoclave charged with sodium carbonate (10.6g), polyethylene glycol-1000 (50g) and methyl ethyl ketone (100 ml) was purged with nitrogen. The mixture was stirred and hexafluoropropene was injected successively until a total pressure drop of 420 psig was recorded, then the temperature was raised to 45° C. and the mixture stirred for a further 4½ hours. The reaction product was filtered and solvent was removed from the filtrate using a rotary evaporator. There remained a pale yellow viscous liquid (58g) which became solid on cooling and standing. Infra-red spectroscopy showed the presence of only a trace amount of unreacted hydroxyl groups and the presence of  $C-F$  bonds and the polyethylene oxide chain in this material. Nuclear magnetic resonance showed the presence of the groups

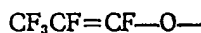


in the ratio 1:4 respectively. The product contained 15.5% fluorine and thus was shown to be a mixture of



### Example 3.

- 5 An autoclave charged with sodium carbonate (10.6g), methyl ethyl ketone (100 ml) and methoxypolyethylene glycol-350 (35g) was purged with nitrogen. The mixture was stirred and hexafluoropropene was injected suc-
- 10 cessively until a total pressure drop of 335 psig was recorded whereupon the temperature was raised to 45° C. for 1½ hours. The reaction product was filtered and solvent was removed from the filtrate using a rotary evaporator.
- 15 There remained a pale yellow liquid (43g) which was shown from hydroxyl group analysis by infrared methods to contain only a trace of unreacted starting material. Nuclear magnetic resonance showed the presence of
- 20 the groups  $\text{CF}_3\text{CFHCF}_2\text{—O—}$  and



- in the ratio 3:1 respectively. From fluorine analysis of 15.3% it was concluded that the fluoroalkyl group was present on one end of
- 25 the polyethylene oxide chain the other end being terminated with a methyl group.

### Example 4.

- 30 An autoclave charged with potassium carbonate (14g), methyl ethyl ketone (100 ml) and polyethylene glycol-1000 (50g) was purged with nitrogen. The mixture was stirred, heated

to 80° C. and tetrafluoroethylene was injected successively until a total pressure drop of 285 psig was recorded whereupon stirring was continued for a further hour and another 5 psig pressure drop occurred. The reaction product was filtered and solvent was distilled from the filtrate using a rotary evaporator. There was obtained a yellow viscous liquid which solidified on cooling and standing. A considerable reduction in the —OH peak height in the infra-red spectrum showed there to be little unreacted starting material. The nuclear magnetic resonance spectrum showed the presence of the group  $\text{HCF}_2\text{CF}_2\text{O—}$  and from an appraisal of all the analytical figures the product was identified as



### Example 5.

50 Reactions between tetrafluoroethylene and hexafluoropropene and several commercially available polyethylene glycols e.g. PEG 600 and PEG 1000 and methoxy PEG 350 were carried out under similar conditions to those described in Examples 1 to 4 and the surface tensions of the products were measured. The results of surface tension measurements made on aqueous solutions of the products at a variety of concentrations are given in Table 1.

60 (The term PEG is an abbreviation for "polyethylene glycol" and the subsequent numeral indicates its approximate molecular weight).

TABLE 1

Product Concentration w/w	Surface Tension (dynes cm <sup>-1</sup> )				
	0.0001	0.001	0.01	0.1	1.0
PEG 1000/C <sub>3</sub> F <sub>6</sub> (Example 1)	58	50	40	29	25
PEG 1000/C <sub>3</sub> F <sub>6</sub> (Example 2)	62	55	43	30	27
PEG 600/C <sub>3</sub> F <sub>6</sub>	58	48	38	28	28
Methoxy PEG 350/C <sub>3</sub> F <sub>6</sub>	68	58	47	35	27
PEG 1000/C <sub>2</sub> F <sub>4</sub> (Example 4)	63	60	57	49	28
PEG 600/C <sub>2</sub> F <sub>4</sub>	68	61	52	46	32
Methoxy PEG 350/C <sub>2</sub> F <sub>4</sub>	70	64	59	51	39

## Example 6.

Comparative tests on the performance of the compounds listed in Table 1 as mould-release agents were conducted. Using a "Beulah" injection moulding machine test mouldings of polypropylene were performed (ICI general purpose grade GWM 100).

The mould selected for the test was a Charpy-2-impression mould made from stainless steel. The compounds were all prepared in the form of an aerosol pack so that each could be readily sprayed as a uniform coating over the interior surface of the mould.

After the internal surface of the mould had been sprayed with one of the compounds as a release agent several mouldings of poly-

propylene were performed until a moulding was observed *not* to be released satisfactorily (i.e. when the moulding was observed to be deformed when ejected from the mould). The number of mouldings performed which were released satisfactorily after each application of release agent was recorded and is shown in Table 2. The mould was cleaned carefully between each set of satisfactory mouldings on one agent before the next agent was applied.

Each release agent was tested in turn as described above and the results are given as Run 1, and then Run 2 was started with the first release agent once more and followed through with the other compounds.

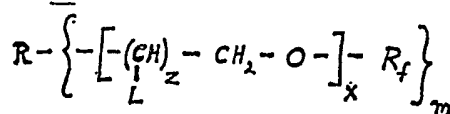
TABLE 2

Product Tested as Release Agent	Test Run Number					
	1	2	3	4	5	6
	Number of Satisfactory Releases					
C <sub>3</sub> F <sub>6</sub> /Methoxy PEG 350	3	3	2	4	3	3
C <sub>3</sub> F <sub>6</sub> /PEG 1000	3	4	6	8	3	3
C <sub>3</sub> F <sub>6</sub> /PEG 300	4	3	3	4	4	4
HC <sub>2</sub> F <sub>4</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>8</sub> CH <sub>3</sub>	5	5	6	7	7	5

C<sub>3</sub>F<sub>6</sub>/PEG 300 (and similarly other products) refers to the reaction product of hexafluoropropene and a polyethylene glycol of molecular weight 300, the reaction being conducted as herein exemplified.

## WHAT WE CLAIM IS:—

1. A compound having the general formula



wherein R<sub>f</sub> is either —CF=CF—(CF<sub>2</sub>)<sub>n</sub>F or —CF<sub>2</sub>—CFH—(CF<sub>2</sub>)<sub>n</sub>F in which n=0 to 10

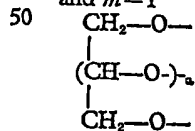
L is H or CH<sub>3</sub>

x is 2 to 40

z is 0, 1 or 2

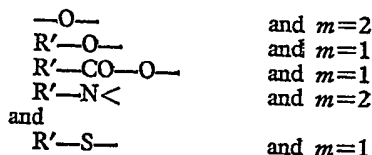
and R and m are selected from

R<sub>f</sub>O— (wherein R<sub>f</sub> is as hereinbefore defined) and m=1



and m=a+2

where a is zero or an integer from one to four.



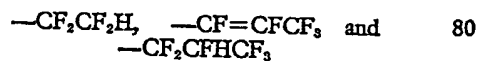
wherein R' is an allyl alkyl, alkyl phenyl or alkyl naphthyl group, the alkyl group in each containing zero, 1 or 2 carbon atoms.

2. A compound as claimed in claim 1 having the formula R<sub>f</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>R<sub>f</sub> wherein x is from 4 to 30.

3. A compound as claimed in claim 1 and having the formula R' O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>R<sub>f</sub> wherein x is from 4 to 30 and R' is an allyl, alkyl alkyl phenyl or alkyl naphthyl group wherein the number of alkyl carbon atoms is zero, 1 or 2.

4. A compound as claimed in claim 3 wherein the group R' is a methyl group.

5. A compound as claimed in any one of the preceding claims wherein the fluoroalkyl group R<sub>f</sub> is selected from the groups



6. A compound substantially as described

herein and as shown in the foregoing examples.

5 7. A method of preparation of a compound as claimed in claims 1 to 6 comprising the reaction of a terminally-unsaturated straight-chain perfluorolefine and a compound containing a chain of repeating oxyalkylene groups terminating in at least one hydroxyl group in the presence of a basic compound.

10 8. A method as claimed in claim 7 wherein the compound containing a chain of repeating oxyalkylene groups consists of a single unbranched chain of the said repeating groups.

15 9. A method as claimed in claim 8 wherein the compound consisting of the single unbranched chain of repeating oxyalkylene groups terminates at one end with the said hydroxyl group and at the other end with a group selected from hydroxyl, alkoxyl, alkyl-phenoxyl, phenoxyl and alkenoxyl.

20 10. A method as claimed in any one of claims 7 to 9 wherein the basic compound is a

sodium or potassium salt of an acid selected from carbonic, phosphoric and silicic acids.

11. A method as claimed in any one of claims 7 to 10 wherein the perfluorolefine is tetrafluoroethylene, hexafluoropropene or a mixture of these two olefines. 25

12. A method as claimed in claim 7 and substantially as described herein with reference to the foregoing examples. 30

13. A surface coating composition comprising a compound as claimed in claims 1 to 6 and a diluent which facilitates the application of the said compound to a surface. 35

14. A composition for use as a release-agent for thermoplastic polymer mouldings comprising a compound as claimed in claims 1 to 6 and an aerosol propellant suitable for the discharge of the composition from an aerosol container. 40

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Agent for the Applicants.

